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Process for the preparation of symmetrical and
asymmetrical carbonates

Description

The present invention concerns the preparation of
symmetrical and asymmetrical carbonates of the general
formula I

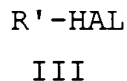
wherein R and R' are the same or different and signify a
straight-chained or branched alkyl group with 1 to 10 C-
atoms, a benzyl group unsubstituted or substituted with up
to three C₁-C₄-alkyl groups, C₁-C₄-alkoxy groups, halogen
atoms, with a cyano group, a nitro group, a trifluoromethyl
group or an alkoxycarbonyl group with up to 4 C-atoms, an
aralkyl group or an alkenyl group. The term aralkyl group
includes a lower alkyl radical with 2 to 10 C-atoms, wherein
up to two H atoms are replaced by phenyl groups, which again
can be substituted with a C₁-C₄-alkyl group, a C₁-C₄-alkoxy
group, a cyano group, a nitro group, a trifluoromethyl
group, an alkoxycarbonyl group with up to 4 C-atoms or with
up to three halogen atoms. The term alkenyl designates an
unsaturated hydrocarbon radical with up to 5 C-atoms.

Organic carbonates play an important role as solvents, as
intermediate products for numerous syntheses and as products

for special fields of use, e.g. in agricultural chemistry or medicinal chemistry (Ullmann's Encyclopedia of Industrial Chemistry, 5th edition, Vol. A5, p. 197, 1986; KIRK-OTHMER, Encyclopedia of Chemical Technology, 3rd ed., Vol. 4, p. 766, 1978; Abbas-Alli G. Shaikh, Chem. Rev. 1996, 96, 951-976).

The preparation of open-chained organic carbonates can e.g. take place (i) from phosgene and hydroxy compounds, (ii) from haloformic acids by reaction with hydroxy compounds, (iii) by alkylation of alkali metal carbonates, (iv) by transesterification of carbonic acid diesters or (v) from carbon dioxide and alcohols under pressure in the presence of catalysts or, however, according to other special processes (H. Hagemann, HOUBEN WEYL, E4, p. 65, 1983; Abbas Alli G. Shaikh, Chem. Rev. 1966, 96, 951).

Processes for the preparation of organic carbonates which avoid the use of the highly toxic phosgene which can use carbon dioxide present and start from simple raw materials are of especial interest from industrial as well as organic-preparative point of view. Stimulated by a work of Ken J. Butcher for the preparation of carbamates from amines and carbon dioxide (Ken J. Butcher, Synlett 1994, 825), it was investigated by us whether alcohols of the general formula II, with use of carbon dioxide, caesium. carbonate and alkyl or aryl halides of the general formula III,



whereby R and R' possess the above mentioned meaning and HAL stands for chlorine, bromine or iodine, can be converted into organic carbonates of the general formula I (scheme 1):

On the basis of the lower nucleophilicity of the OH group in alcohols in comparison with the NH_2 group in amines and on the basis of the special methods described in the literature for the preparation of carbonates from carbon dioxide (Abbas-Alli G. Shaikh, Chem. Rev. 1996, 951, 966), a synthetic access to carbonates with use of the system carbon dioxide/caesium carbonate at low temperatures was not to be expected.

Surprisingly, however, it was found that organic carbonates of the general formula I can be prepared under very mild and preparatively simple conditions in the presence of alkali metal carbonates, especially caesium carbonate, from alcohols of the general formula II and alkyl or aryl halides of the general formula III. For this reaction, surprisingly no further catalyst is necessary. The preparative procedure is as follows:

The alcohol and a 2 to threefold molar excess of caesium carbonate are placed in a suitable dipolar aprotic solvent, such as e.g. dimethylformamide, acetonitrile, dimethylacetamide or N-methylpyrrolidone, at room temperature. With good stirring, carbon dioxide gas is now passed at room temperature, with exclusion of moisture, for 4 to 6 hours into the reaction mixture (about 5 bubbles/second). The carbon dioxide is hereby produced by allowing dry ice to evaporate which is present in an Erlenmeyer flask which is connected with the reaction vessel via a gas inlet pipe. One now adds to the reaction mixture in one portion 1 equivalent (referred to the alcohol) of the alkyl or aryl halide in question of the general formula III, dissolved in a little solvent, passes further carbon dioxide in for 1 hour, again adds thereto 5-100%, preferably 10%, of the original amount of alkyl or aryl halide and then closes the reaction vessel. With closed reaction vessel, one now

stirs further for 24 hours to 3 days at room temperature. Thereafter, one pours the reaction mixture on to water, extracts the product with ethyl acetate and purifies the so obtained raw product with the methods usual in preparative organic chemistry, e.g. by chromatography or crystallisation. Preferred solvent for the described reaction is dimethylformamide.

The reaction conditions are very mild, there are tolerated many functional groups, such as e.g. the double bond, the nitro group, the alkoxycarbonyl group, the cyano group, halogen groups and alkoxy groups on aromatics. The starting materials - alcohols and alkyl and aryl halides - are simple to prepare and are commercially available in large number. The conditions for the working up of the reaction are very easy to produce. With the assumption that caesium carbonate can again be prepared from the extracted aqueous residue, the method is suitable to bind gaseous carbon dioxide on to simple commercially available starting materials, such as alcohols and alkyl or aryl halides and thereby to produce valuable, energy-rich intermediate products. In this sense, the said process is a valuable addition to an environmentally friendly chemistry.

Because of the simplicity of the process, the method of procedure is also suitable as basis for a high throughput synthesis. For this purpose, in a carbon dioxide gasification apparatus which contains DMF solutions of corresponding alcohols, would have to be gassed with CO₂ for some hours. Thereafter, the corresponding alkyl or aryl halides are to be dosed thereto, the vessel to be closed and to be stirred for 24 hours to 3 days at room temperature. Thereafter, the carbonates formed are to be isolated in simple manner.

The invention is illustrated and explained by the following embodimental Examples.

Example 1

Dibenzyl carbonate from benzyl alcohol and benzyl 5 bromide

Into a suspension of 0.45 g benzyl alcohol and 3.0 g caesium carbonate in 30 ml dry dimethylformamide, which is present in a 50 ml three-necked flask, carbon dioxide gas is passed for 4 hrs, with good stirring at room temperature. One adds thereto 0.7 g benzyl bromide dissolved in a little DMF, passes in further carbon dioxide for 1 hr., again mixes with 0.1 g benzyl chloride and then closes the reaction vessel airtight. The reaction mixture is now further stirred for 2 days at room temperature. Thereafter, one pours the reaction mixture on to 50 ml water (care: exothermic reaction) and extracts the product 3 times with, in each case, 50 ml ethyl acetate. The organic phase is dried over sodium sulphate, filtered and evaporated on a rotavapor. The dimethylformamide present in the oily residue, together with the product, is removed on the rotavapor by azeotropic distillation by means of toluene at 40 mbar/50°C. The residue is chromatographed on 130 g silica gel (0.040 - 0.063) with toluene as elution agent. One obtains 0.95 g of product. M.p. 30 - 31°C.

The following Examples are carried out analogously to Example 1 (reaction time in hours/yield):

Example 2

Benzyl 2-phenylethyl carbonate, oil
from 2-phenyl-ethanol and benzyl bromide
48/93%

Example 3

Benzyl ethyl carbonate, oil,
from benzyl alcohol and ethyl bromide

18/73%

Example 4

Benzyl tert.-utyl carbonate,
oil, from tert.-butanol and benzyl bromide
120/15%

Example 5

Di-Benzo[b]furan-2-yl methyl carbonate, oil,
from 2-hydroxymethylbenzo[b]furan
120/23%

Example 6

Benzyl 3-phenylpropyl carbonate, oil,
from 3-phenylpropanol and benzyl bromide
120/99%

Example 7

Benzyl 4-chlorobenzyl carbonate, oil,
from benzyl alcohol and 4-chlorobenzyl chloride
64/50%

Example 8

Benzyl 4-methoxybenzyl carbonate, oil,
from benzylalcohol and 4-methoxybenzyl chloride
88/64.4%

Example 9

Benzyl 4-methylbenzyl carbonate, oil,
from benzyl alcohol and 4-methylbenzyl chloride
64/52.3%

Example 10

Benzyl 2,4-dichlorobenzyl carbonate, oil,
from benzyl alcohol and 2,4-dichlorobenzyl chloride

64/49%

Example 11

4-Chlorobenzyl 2-phenylethyl carbonate, oil,
from 2-phenylethanol and 4-chlorobenzyl chloride

64/32.7%

Example 12

Di-4-methoxybenzyl carbonate, m.p. 73°C,
from 4-methoxybenzyl alcohol and 4-methoxybenzyl chloride

88/72%

Example 13

Di-2,4-dichlorobenzyl carbonate, oil,
from 2,4-dichlorobenzyl alcohol and 2,4-dichlorobenzyl
chloride

64/70.5%

Example 14

Di-4-methylbenzyl carbonate, m.p. 55°C,
from 4-methylbenzyl alcohol and 4-methylbenzyl bromide

88/40%

Example 15

Di-4-chlorobenzyl carbonate, m.p. 94°C,
from 4-chlorobenzyl alcohol and 4-chlorobenzyl bromide

64/78.3%

Example 16

Di-4-chlorobenzyl carbonate, m.p. 97°C,
from 4-chlorobenzyl alcohol and 4-chlorobenzyl chloride

64/54.8%

Example 17

(±)-Benzyl-2-methyl-2-phenylethyl carbonate, oil,
from (±)-2-methyl-2-phenylethyl alcohol and benzyl bromide
64/63.1%

Example 18

Benzhydryl benzyl carbonate, m.p. 72°C,
from benzhydrol and benzyl bromide
64/71.2%

Example 19

(±)-Benzyl 1-phenylethyl carbonate, oil, from (±)-1-
phenylethanol and benzyl bromide
64/57.1%

Example 20

Benzyl 3-phenylpropyl carbonate, oil,
from 3-phenyl-propanol and benzyl bromide
120/99%

Example 21

(±)-Benzyl 1-methyl-2-phenylethyl carbonate, oil,
from (±)-1-phenyl-2-propanol and benzyl bromide
120/99%

Example 22

Benzyl 4-methoxycarbonylbenzyl carbonate, m.p. 53°C,
from 4-methoxycarbonylbenzyl alcohol and benzyl bromide
120/65%

Example 23

Di-4-nitrobenzyl carbonate, m.p. 167° - 168°C,
from 4-nitrobenzyl alcohol and 4-nitrobenzyl bromide
64/77%

Example 24

Benzyl benzo[b]furan-2-ylmethyl carbonate, m.p. 59° - 60°C,
from 2-hydroxymethylbenzo[b]furan and benzyl bromide
64/100%

Example 25

Benzyl 4-cyanobenzyl carbonate, m.p. 54°C,
from benzyl alcohol and 4-cyanobenzyl bromide
64/100%

Example 26

Benzyl 3-trifluoromethylbenzyl carbonate, oil,
from benzyl alcohol and 3-trifluoromethylbenzyl bromide
48/100%

Example 27

Benzyl 1-phenylethyl carbonate, oil, from benzyl alcohol and
1-phenylethyl bromide
64/66%

Example 28

Di-2-phenylethyl carbonate, m.p. 56°C,
from 2-phenyl-ethanol and 2-phenylethyl bromide
64/69.4%

Example 29

Di-3-phenylpropyl carbonate, oil, from 3-phenylpropanol
and 3-phenylpropyl bromide
64/98%

Example 30

Benzyl tert.-utyl carbonate, oil,
from benzyl alcohol and tert.-utyl bromide
64/7%

Example 31

Benzyl 4-Nitrobenzyl carbonate, m.p. 68°C,
from benzyl alcohol and 4-nitrobenzyl bromide
64/93%

Example 32

Allyl benzyl carbonate, oil,
from benzyl alcohol and allyl bromide
64/80%

Example 33

Allyl benzyl carbonate, oil,
from allyl alcohol and benzyl bromide
64/70%

Example 34

Benzyl cinnamyl carbonate, oil,
from cinnamyl alcohol and benzyl bromide
64/74.5%

Example 35

(±)-Benzyl 1-methylpropyl carbonate, oil,
from (±)-1-methylpropanol and benzyl bromide
64/58%

Example 36

Benzyl butyl carbonate, oil,
from n-butanol and benzyl bromide
48/58.5%

Example 37

Benzyl 4-nitrobenzyl carbonate, m.p. 68°C,
from 4-nitro-benzyl alcohol and benzyl bromide
64/80.6%